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<p>(54) Title: <b>PULP BLEACHING</b></p> <p>(57) Abstract</p> <p>Bleach activators are reacted with the peroxygen source in aqueous solution at an acidic pH to form an oxidising product which is a stronger oxidising agent than the peroxygen source used as a starting material. The product solution is used in a delignifying and/or bleaching process for cellulosic pulps. The activator is preferably solid at room temperature. The activator and peroxygen source may be reacted in the presence of the pulp to provide the stronger oxidising agent.</p>		

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PULP BLEACHING

The present invention relates to a process for bleaching of cellulosic pulps, especially for use in paper making, in which an activator is used during a peroxide bleaching step carried out at a pH which is acidic or slightly alkaline. The process is usually part of multi-step process, especially a chlorine free pulp bleaching process.

The use of chlorine and even chlorine dioxide in bleaching processes for pulps causes environmental problems due to production of polychlorinated organic compounds in the paper and the waste. Pulp bleached with totally chlorine free sequences (TCF) is being manufactured and sold by many pulp mills. In TCF bleaching, the pulp is first delignified as much as possible with existing cooking and oxygen pre-delignification facilities. The pulp is then treated in several bleaching stages, optionally preceded by a sequestering stage to remove heavy metals from the pulp. Heavy metals otherwise tend to increase the rate of decomposition of peroxygen bleaching moieties. The multi-step bleaching processes may include steps carried out under acidic and/or alkaline processes. Although the mechanical properties of the paper from pulps produced by TCF processes are satisfactory, the final brightness is often inadequate, and the paper has poor brightness reversion properties so that it tends to yellow after a time.

Alkaline peroxide bleaching steps carried out in the presence of a bleach activator compound have been described. The Peramid process (trade mark) marketed by SKW Trostberg uses a cyanamide, usually an acetyl cyanamide, as an activator, as described in US-A-5,034,096, EP-A-0,479,319, CA 1,277,457 (& EP-A-0,226,114), DE-A-4,004,364, DE-A-4,114,134 and DE-A-4,114,135.

Other organic compounds have been suggested as additives for alkaline peroxide bleaching steps.

EP-A-0,543,174 suggests the use of sodium cyanate in an alkaline peroxide step. US-A-3,687,803 suggests the inclusion of an activator which is a benzoyl chloride, though the pH is usually 8.5 or higher. US-A-3,193,445 describes a two-stage procedure in which pulp is treated with hydrogen peroxide under alkaline conditions to at least partially deplete the peroxide, after which acetic anhydride is added directly to the product of the first stage to continue the bleaching. In WO-A-88/06202 carboxylic acids are added to alkaline hydrogen peroxide.

In EP-A-0456032 a pulp bleaching process is described in which pulp is bleached with a peroxide and a bleach activator such as TAED, under alkaline conditions. The highest bleaching effect is said to be obtained at pH 9-10. In JP-05-186989 oxygen gas or peroxides are added to an aqueous alkaline slurry of cellulose pulp. The treatment is conducted in the presence of an amine acylation product. The alkali is preferably added on a bone-dry pulp weight basis 0.5-3% as  $\text{Na}_2\text{O}$ , preferably sodium hydroxide is used.

In JP-A-(1989)-104893 long chain alkanoyloxy-benzene sulphonate activators are used to enhance the activity of various alkaline bleaches including peracetic acid and hydrogen peroxide.

Acidic bleaching steps using percarboxylic acids have been described, for instance using performic acid or peracetic acid. Both these acids are themselves unstable. In order to avoid having to transport the percarboxylic acid, it is known to make the acid at the pulp mill in a previous preparation stage. For instance in DE-A-2,219,505 an equilibrium peracid is used, made by adding an excess of carboxylic acid to hydrogen peroxide. It is also suggested to use the anhydrides instead of the acids to form the peracid in this process. In DE-A-3,005,947, it is suggested to use very high concentration organic acid in concentrated hydrogen peroxide to form the peracid. In DE-A-4,114,134 peracetic acid is made by the reaction of acetic acid and hydrogen peroxide in the presence of

concentrated sulphuric acid. In all these processes the amount of water must be kept relatively low in order that the equilibrium is driven to maximise the amount of peracid formed. Any reaction must thus take place in a separate stage outside the bleach tower. Also, the higher the concentration, the more precautions are needed for handling the materials.

GB-A-1,117,336 describes an apparatus and process for making peracetic acid on the site where the solution is required as a bleaching agent by reaction of acetic anhydride and hydrogen peroxide in the presence of a basic catalyst.

The Milox pulping process involves the cooking of woodchips with hydrogen peroxide in the presence of formic acid or acetic acid. In the process it is believed that the corresponding percarboxylic acid is formed and acts as the active oxidising agent. It has been suggested to use the Milox process steps also to treat pulp produced by other pulping processes (such as Kraft) as a delignification stage prior to subsequent bleaching stages.

In WO-A-86/05529 it is suggested to produce the peracid by reaction of aldehyde with molecular oxygen.

Troughton et al, from Solvay Interlox, in a paper presented to The International Non-Chlorine Bleaching Conference, March 6-10, 1994 Amelia Island, Florida, USA, describe multi-stage bleaching processes for TCF kraft pulps, including an initial sequestration stage, followed by multiple peroxide bleaching stages and optional peracid bleaching stages. The peracids used are permono sulphuric acid or Caro's acid and percarboxylic acid. Troughton et al propose distilling peracetic acid to minimise waste of unreacted acetic acid and hydrogen peroxide. Concentrating the peracid in this way, however increases handling difficulties. It is suggested that the pH of the pulp during a peracid bleaching stage should be low, because of the rapid rate of decomposition of the peracid around the pKa of the peracid. It is also indicated that the initial

rate of delignification by the peracid is increased at higher pH, but the competing decomposition reaction (forming oxygen gas) means that around half of the peracid may be lost to this side reaction. The desirability of having a peracid stage between two alkaline peroxide stages is explained as allowing residual lignin resistant to alkaline peroxide from the first alkaline peroxide bleaching step to be attacked to generate phenolic hydroxyl groups, which can subsequently be attacked in the following alkaline peroxide stage.

In US-A-3227655, formation of a peracetic acid bleach solution from hydrogen peroxide and acetic anhydride is described. The bleach solution may be prepared at a concentration for immediate bleaching or as a concentrate for dilution, under acidic conditions.

However, many of the known pulp bleaching processes are unsatisfactory because they produce pulps which have poor brightness reversion properties so that over time, after bleaching and even after manufacturing into a cellulosic product, yellowing tends to occur. This is particularly so for TCF processes. Overcoming this problem may reduce fibre strength and this is a particular problem for recycled paper.

There is therefore still a need for an improved pulp bleaching process which will overcome these problems.

The new process according to the present invention for bleaching cellulosic pulps comprises the steps:

- a) forming an aqueous solution containing hydrogen peroxide or an inorganic persalt and a bleach activator compound which is an acyl donor to form an oxidising compound which is a stronger oxidising agent than hydrogen peroxide, the step being carried out at a pH in the range 1 to  $pK_a'$ ;
- b) contacting the pulp with the stronger oxidising agent at a starting pH in the range 1 to  $pK_a'$  where  $pK_a'$  is the  $pK_a$  of the percarboxylic acid corresponding to the acyl group of the activator,

in which the bleach activator compound is selected from N-acyl and O-acyl derivatives, and wherein when the activator compound is an anhydride it is a solid material.

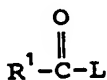
The invention also includes a process for bleaching cellulosic pulps comprising the steps:

(a) forming an aqueous solution containing hydrogen peroxide or an inorganic persalt and a bleach activator compound which is an acyl donor to form an oxidising compound which is a stronger oxidising agent than hydrogen peroxide, the step being carried out at a pH in the range 1 to  $pK_a'$ ;

(b) contacting the pulp with a stronger oxidising agent at a starting pH in the range 1 to  $pK_a'$  where  $pK_a'$  is the  $pK_a$  of the percarboxylic acid corresponding to the acyl group of the activator, in which the bleach activator compound is selected from N-acyl and O-acyl derivatives, and the hydrogen peroxide or inorganic persalt and the bleach activator compound are added directly to the pulp, either simultaneously or one after the other, the oxidising compound forming in the presence of the pulp.

The present invention is particularly advantageous because it has been found to produce pulps having good brightness reversion properties without the usual increase in fibre damage.

Preferably the activator is a compound of the formula I



I

in which L is a leaving group attached via an oxygen or a nitrogen atom to the C=O carbon atom and  $\text{R}^1$  is an alk(en)yl, aralkyl, alkaryl, or aryl group, any of which groups has up to 24 carbon atoms and may be substituted or unsubstituted.

The leaving group L is preferably a compound the conjugate acid of which has a  $pK_a$  in the range 4 to 13, preferably 7 to 11, most preferably 8 to 11.

It is preferred that  $R^1$  is an aliphatic group preferably a  $C_{1-18}$  alkyl group, or an aryl group.

In the present invention the alk(en)yl groups may be straight, branched or cyclic.

5 In the formula I L and  $R^1$  may be joined to form a cyclic compound, usually a lactone or a lactam. These cyclic groups may include heteroatoms, for instance oxygen or optionally substituted nitrogen atoms, carboxyl groups as well as  $-CH_2-$  groups or substituted derivatives thereof.  
10 They may be saturated or unsaturated. L can itself comprise a cyclic group, including heterocyclic groups, for instance joined to the  $C=O$  group of the compound I via the heteroatom.

Substituents on  $R^1$  and L can include hydroxyl,  
15  $=N-R^2$  in which  $R^2$  is selected from any of the groups represented by  $R^1$  and is preferably lower alk(en)yl, amine, acyl, acyloxy, alkoxy, aryl, aroyl, aryloxy, aroyloxy, halogen, amido, and imido groups and the like as well as other groups not adversely affecting the activity of the  
20 compound.

In the invention the compound of the formula I can be any N-acyl or O-acyl acyl-donor compound, which has been described as a bleach activator for use in laundry detergents. The compound of the formula I may be an  
25 anhydride, but is preferably an ester or, even more preferably, an amide derivative.

Amide derivatives include acyl imidazolides and N,N-diacylamides. Other examples of N-acyl derivatives are:

- a) 1,5-diacetyl-2, 4-dioxohexahydro-1,3,5-triazine  
30 (DADHT);  
b) N-alkyl-N-sulphonyl carbonamides, for example the compounds N-methyl-N-mesyl acetamide, N-methyl-N-mesyl benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide;  
35 c) N-acylated cyclic hydrazides, acylated triazoles or urazoles, for example monoacetyl maleic acid hydrazide;

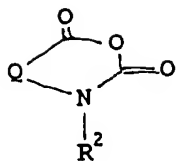


- d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl hydroxylamine and O,N,N-triacetyl hydroxylamine;
- e) N,N'-diacyl sulphurylamides, for example N,N'-dimethyl-N,N'-dimethyl-N,N'-diacetyl sulphuryl amide and N,N'-diethyl-N,N'-dipropionyl sulphurylamide;
- f) 1,3-diacyl-4,5-diacyloxy-imidazolines, for example 1,3-diformyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-dipropionyloxy imidazoline;
- g) Acylated glycolurils, such as tetraacetyl glycoluril and tetrapropionyl glycoluril;
- h) Diacylated 2,5-diketopiperazines, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and 1,4-dipropionyl-3,6-dimethyl-2,5-diketopiperazine;
- i) Acylation products of propylene diurea and 2,2-dimethyl propylene diurea, especially the tetraacetyl or tetrapropionyl propylene diurea and their dimethyl derivatives;
- j) Alpha-acyloxy-(N,N')polyacyl malonamides, such as alpha-acetoxy-(N,N')-diacetyl malonamide.
- k) O,N,N-trisubstituted alkanolamines, such as O,N,N-triacetyl ethanolamine.
- k') Cyanamides, such as those disclosed in DE-A-3,304,848.
- l) N-acyl lactams, such as N-benzoyl-caprolactam, N-acetyl caprolactam, the analogous compounds formed from C<sub>4-10</sub> lactams.
- m) N-acyl and N-alkyl derivatives of substituted or unsubstituted succinimide, phthalimide and of imides of other dibasic carboxylic acids, having 5 or more carbon atoms in the imide ring.
- Alternatively the compound may be an ester, for instance
- n) sugar esters, such as pentaacetylglucose,
- o) esters of imidic acids such as ethyl benzimidate,
- p) triacylcyanurates, such as triacetylcyanurate and tribenzoylcyanurate,

- q) esters giving relatively surface active oxidising products for instance of  $C_{8-18}$ -alkanoic or -aralkanoic acids such as described in GB-A-864798, GB-A-1147871 and the esters described in EP-A-98129 and EP-A-106634, for instance compounds of the formula I where L comprises an aryl group having a sulphonic acid group (optionally salified) substituted in the ring to confer water solubility on a benzyl group, especially nonanoyloxy-benzenesulphonate sodium salt (NOBS), isononanoyloxy-benzenesulphonate sodium salt (ISONOBS) and benzoyloxy-benzenesulphonate sodium salt (BOBS)
- r) phenyl esters of  $C_{14-22}$ -alkanoic or -alkenoic acids,
- s) esters of hydroxylamine,
- t) geminal diesters of lower alkanolic acids and gem-diols, such as those described in EP-A-0125781 especially 1,1,5-triacetoxypent-4-ene and 1,1,5,5-tetraacetoxypentane and the corresponding butene and butane compounds, ethylidene benzoate acetate and bis(ethylidene acetate) adipate and
- u) enol esters, for instance as described in EP-A-0140648 and EP-A-0092932.

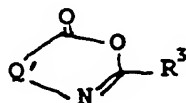
Where the activator is an anhydride it is preferably a solid material, and is preferably an intra-molecular anhydride, or a polyacid polyanhydride. Such anhydride compounds are more storage stable than liquid anhydrides, such as acetic anhydride. Anhydride derivatives which may be used as activator include

- v) intramolecular anhydrides of dibasic carboxylic acids, for instance succinic, maleic, adipic, phthalic or 5-norbornene-2,3-dicarboxylic anhydride,
- w) intermolecular anhydrides, including mixed anhydrides, of mono- poly-basic carboxylic acids, such as diacetic anhydride of isophthalic or perphthalic acid
- x) isatoic anhydride or related compounds such as described in WO-A-8907640 having the generic formula II



II

5 wherein Q is a divalent organic group such that Q and N together with the carbonyl groups and oxygen atom of the anhydride group form one or more cyclic structures and R<sup>2</sup> is H, alkyl, aryl, halogen or a carbonyl group of a  
10 carboxyl containing function; or benzoxazin-4-ones as described in WO-A-8907639, that is compounds of the formula III



III

15 wherein Q' is selected from the same groups as Q and R<sup>3</sup> is H, alkyl, aryl, alkaryl, aralkyl, alkoxyl, haloalkyl, amino, aminoalkyl, carboxylic group or a carbonyl-  
20 containing function; preferably 2-methyl-(4H)3,1-benzoxazin-4-one (2MB4) or 2-phenyl-(4H)3,1-benzoxazin-4-one (2PB4);  
y) polymeric anhydrides such as poly(adipic) anhydride or  
25 other compounds described in WO-A-9306203.

In the present invention a mixture of activators may be utilised. For instance it may be desirable to use a mixture of activators which will provide different oxidising compounds, such compounds preferably having  
30 different hydrophilicities. For instance it may be desirable to use a mixture of activators which will provide a relatively hydrophobic oxidising compound and a relatively hydrophilic oxidising compound. Such mixtures of activators are described in our earlier patent  
35 publication EP-A-0299599. In such mixtures, in the formula I, the two activators will have different R<sup>1</sup> groups and may have the same or different leaving groups L. For instance one of the groups R<sup>1</sup> may be a methyl group, so as to form peracetic acid. The other of the groups R<sup>1</sup> may comprise a

higher alkyl group, for instance a  $C_{6-12}$ -alkyl, optionally branched alkyl.

The process of the present invention, that is either or both of steps a) and b), may be carried out in the presence of a bleach catalyst. Suitable bleach catalysts are for instance, manganese complex based catalysts or polyoxometalates, as recently promoted by Kemira, as well as organic catalysts such as enzymes and sulphonamines.

In the process of the invention the step a) may be carried out before step b). For instance the hydrogen peroxide or inorganic persalt and the bleach activator may be allowed to react in aqueous conditions for at least 5 minutes preferably 10 minutes, up to one or two days, preferably one day, before the aqueous reaction product of step a) is added to the aqueous pulp. Alternatively hydrogen peroxide or persalt and the bleach activator compound may be added direct to the pulp, either simultaneously or one after the other, optionally with a period of time between separate additions. Where the peroxide or persalt and bleach activator are pre-reacted, the reaction is preferably carried out at a temperature, in the range 10-60°C, most preferably in the range 20-40°C.

The concentration of hydrogen peroxide in step a) reaction mixture is preferably in the range 0.1% to 60%, usually in the range 0.2 or 0.5% to 30 or 10% w/v. Inorganic persalt, which is less preferred, can be used in a concentration to give the same amount of available oxygen in a given volume of solution as the specified preferred concentrations of hydrogen peroxide. The bleach activator is preferably present in step a) and step b) in an amount to provide 0.1 to 5.0 mole equivalents, preferably 0.2 to 1.0 mole equivalents, of acyl groups compared to peroxide. The pH is suitably in the range 2 to  $(pK_a' - 0.05)$ , more preferably  $(pK_a' - 3)$  to  $(pK_a' - 0.2)$ .

The pH in the step b) is at or below  $pK_a'$  and is preferably in the range  $(pK_a' - 5)$  -  $(pK_a' - 0.1)$  most preferably in the range  $(pK_a' - 2)$  to  $(pK_a' - 0.5)$ . The

solution of step a) may be diluted before step b) if the steps are carried out in that order. The  $pK_a$  of some of the peracids corresponding to the acyl group of the activator are as follows: Peracetic:8.2; Performic:7.1; 5 Perbenzoic:7.64 perbutanoic:8.2; perpropanoic:8.1. Use of a pH too far below  $pK_a$  should be avoided because the rate of bleaching is too slow.

The mixture of peroxide and activator may be made up in either order, that is by formation of a peroxide 10 solution followed by addition of activator or vice versa. Where the activator is a solid best results have been obtained by predissolution of the activator in water if necessary at elevated temperature followed by mixing with peroxide solution, then adjusting pH.

15 The process is suitable for use as one stage in a multi-stage process, especially for providing totally chlorine free pulp. It may also be of use where the total process is free of elemental chlorine (or molecular chlorine or chlorine gas), that is where the process 20 includes a chlorine dioxide bleaching step. Such a step may be carried out before or after the steps of the present invention.

The present invention is particularly suitable for use following steps in which the pulp has been at least 25 partially delignified. Such previous delignification and/or bleaching stages may be carried out, for instance, by peroxide under alkaline conditions or acidic conditions, oxygen and/or ozone treatment steps or peracid acid treatment steps, as well as any of the other 30 delignification steps. The pulp may be any type of pulp including mechanical, but is preferably chemical pulp.

The process of the present invention has been found to be of particular value where the process involves a subsequent alkaline peroxide bleaching stage. Since the 35 process of the present invention is carried out at higher pH's than conventional peracid bleaching stages, the amount of alkaline chemical required to be added subsequently to

achieve the desired alkaline pH is reduced and may be dispensed with altogether in some cases. A subsequent alkaline bleaching step is usually carried out by contacting the pulp treated by the process of the present invention with hydrogen peroxide or another bleach, preferably an oxygen bleach, under alkaline conditions, preferably at a pH in the range 9 to 12, and optionally in the presence of an activator and/or sequestrant. The alkaline bleaching step may be carried out after an intermediate rinsing step for instance where such a rinse step removes dissolved components which would otherwise react with reagents for subsequent steps, thereby deactivating them before they can interact with the pulp. Such interstage rinses may also remove transition metals liberated during the acidic bleaching step of the present invention which could cause decomposition of the bleach in a subsequent alkaline bleaching stage. A subsequent alkaline bleaching stage may be carried out without an intermediate rinsing step. The pulp may be thickened prior to the subsequent alkaline peroxide or other alkaline bleaching step.

The present inventors have discovered that the bleaching step of the present invention is of particular value as the penultimate step of the overall bleaching process. The present invention thus preferably comprises a single alkaline peroxide bleaching step following the novel activated bleach step.

The novel process of the present invention may also be used to bleach or otherwise treat recycled pulp, including recycled deinked pulp, or as a combination deinking/bleaching step.

It is preferred that the pulp contacted with the stronger oxidising agent in step b) of the present invention should be relatively free of potentially interfering heavy metal or transition metal ions. Such ions might otherwise catalyse premature decomposition of oxidising species. Where step b) of the present invention

is carried out at a relatively late stage of multi-stage bleaching process, it may be unnecessary to take measures to remove transition metals from the pulp, especially where there has been a previous acid step in the pulping or delignification/bleaching steps. If, however, the pulp retains relatively high quantities of heavy metal ions, these can be removed in a previous step in which the pulp is contacted with a suitable organic sequestrant. For such steps it may be preferably to remove the sequestered heavy metal with the supernatant liquor.

Alternatively it may be possible to add heavy metal sequestrants to the pulp itself in step b) of the process according to the present invention so that sequestered heavy metal remains dissolved in the system during the bleaching process. Suitable sequestrants for remaining in the system are usually phosphonic acid or carboxylic acid derivatives, selected having regard to the pH and the metal ions to be sequestered. Examples are ethylene diamine tetraacetic acid (EDTA) and diethylene triamene pentacetic acid (DTPA) or poly(methylene phosphonic acid) derivatives such as ethylene diamine tetra methylenephosphonic acid (EDTMP). Heavy metals, when sequestered by such compounds appear to be inactivated and do not cause decomposition of the stronger oxidising species.

The present inventors have discovered that the process of the present invention is of particular utility where the incoming pulp has a brightness of less than 85% ISO (that is has a value of less than 85% when tested by International standard test method at 457 nm using a Carlzeiss Elrepho). The brightness of the incoming pulp is preferably in the range 83-85%.

The process of the present invention is preferably carried out a temperature of at least 40°C, preferably less than 95°C, more preferably in the range 60-80°C. The step is generally carried out for a period of time sufficient to reduce the kappa number of the pulp (as determined by International standard test method number ISO 302) of at

least 10%, preferably at least 20%. The reaction is generally carried out over a period in the range 10 min to 6 hours, preferably at least 20 minutes up to three hours, for instance 30 minutes to 120 minutes.

5       The present invention is desirable for several reasons and has many advantages over the prior art. Although the reaction may be carried out in a holding tank, the components for the bleaching step may also be prior mixed immediately before addition to the bleaching tower, thus  
10       requiring no additional reaction vessel or holding tank. This flexibility provides a more convenient process than prior art processes in which peracetic acid is formed in situ from acetic acid or acetic anhydride and hydrogen peroxide. Compared with processes in which hydrogen  
15       peroxide itself is used as the bleach, the use of an activator provides improved bleaching results, whilst allowing operation at lower temperatures. Mixtures of bleaching agents, that is of "stronger oxidising agents" can be provided by the use of mixtures of activators. This  
20       is not possible with existing processes using peracetic acid. The provision of mixed oxidising species may allow simultaneous bleaching of components of the pulp more susceptible to one or other of the species. In particular the use of a mixture of activators providing relatively  
25       hydrophobic and relatively hydrophilic bleaching species may allow penetration of bleaching agents into relatively hydrophobic sites in the pulp not previously possible with peracetic acid alone, whilst retaining the desirable performance of a relatively hydrophilic oxidising species  
30       such as peracetic acid. Furthermore it is easier to control the pH of liquor in the bleaching tower using the present invention than is the case when using prior art peracetic or Caro's acids. In addition the amount of activator added can be adjusted to adjust the extent of  
35       bleaching, for different sources of wood, or to give different degrees of bleaching, the present invention being more flexible and adaptable than the use of preformed



peracids. The concentration of actives and the rate of release of strong oxidising species can be controlled by changing the temperature in the bleach tower, altering the pH or altering the peroxide to activator ratio. For preformed peracids the concentration of actives can only be changed by dilution. However dilution causes decomposition of the peracids by moving the equilibrium back to peroxide and acid. Furthermore by optimising conditions in the process of the present invention essentially all the activator present may be productively consumed. Optionally this may be by recycling unreacted activator to form part of the starting materials for the bleaching step. Since the use of an activator allows the solutions created and the bleaching process itself to be carried out at relatively dilute concentrations, this minimizes handling problems otherwise encountered with prior art processes using peracetic acid.

Surprisingly the process of the invention provides treatment pulp, in which the product paper has better resistance to yellowing than prior art processes which do not use an activator. Furthermore the final brightness obtained using the process of the present invention is improved without any increase in the amount of fibre damage.

The invention is illustrated further in the following examples.

#### Pulps

The following three pulps were subjected to tests:

- Pulp 1 - a soft wood kraft pulp subjected to initial peroxide bleaching steps to give a brightness of 82.5%, kappa number 5.1 and viscosity of 780 dm<sup>3</sup>/kg.
- Pulp 2 - a hard wood kraft pulp bleached by previous peroxide bleaching steps to give brightness 83.0%, kappa number 6/1 and viscosity 670 dm<sup>3</sup>/kg.
- Pulp 3 - a second soft wood kraft pulp subjected to previous steps of peroxide bleach to give a brightness of 85.1%, kappa number 2.1% and viscosity 610 dm<sup>3</sup>/kg

### Chelation Stage

Optimisation of a chelation stage carried out prior to the bleaching stage under test was carried out to select the optimal chelating agent (either diethylene triamine penta acetic acid (DTPA) or diethylenetriamine penta(methylene phosphonic acid) (DTPMP)), the dosage, the time and the pH at which chelation takes place. The chelation was carried out at concentrations of chelating agent in the range 0.1 to 0.3 % on pulp for DTPA and 0.05 to 0.8% on pulp for DTPMP. The pH was 4.5 or 6 or DTPA or 6 for DTPMP. The consistency of the pulp was 2% and the temperature was 70°C, the reaction time being 60 minutes. Following the chelation step the pulp slurry was concentrated and washed.

### Preparation of Activator-Peroxide Solution

A solution containing hydrogen peroxide and tetracetylene diamine (TAED) was made up by first dissolving an appropriate amount of TAED into water at 70-80°C, then adding an appropriate amount of aqueous hydrogen peroxide and adjusting pH as necessary. It was used immediately in an amount so as to give the dosage mentioned in the tables below.

### Bleaching Stage

The pulp having been subjected to the previous chelation stage, was adjusted to the desired pH (in the range 2 to 8) and temperature (60 or 80°C) and then a suitable quantity of the solution of TAED/peroxide was added to the pulp together with any other ingredients as specified in the tables. The mixture was allowed to react with intermittent stirring. The properties of pulp after reaction times of thirty minutes up to 360 minutes were determined. For some processes a subsequent alkaline bleaching step was conducted. The pulp from the novel bleaching step of this invention was then subjected to a number of tests. The following tests were used:

**Pulp Testing**

1. The brightness of the pulp was determined as the brightness of a split sheet at a wavelength of 457nm. The apparatus used was a Carl Zeiss Elrepho
2. Kappa number was determined according to the standard ISO 302.
3. Pulp viscosity was determined according to the standard SCAN-CM 15:88.
4. The light scattering coefficient of the pulp was determined according to the standards ISO 5269/1 and SCAN C 27:76. The light absorption coefficient was calculated on the basis of this determination.
5. The post-color value PC,a was determined at 100°C and 100% relative humidity after one hour TAPPI standard T260 om-85.
6. The post-color value PC,b was determined at 105°C after 24 hours.
7. The post-color value PC,c was determined after irradiation in a Xenotester for three hours.
8. The physical properties of the paper sheets made from pulp were determined according to the standards ISO 5264/2, ISO 5269/1, ISO 5267/1, ISO 5270 and SCAN C 27:76. Brightnesses before and after were determined at 457nm with an Elrepho 2000.

**Results**

The conditions selected for the chelation stage as suitable for all three pulps was found to utilise DTPMP at a concentration of 0.2% and at a pH of 6.

The results of the peroxide bleaching under the various conditions is set out in the Tables 1 to 7. In Figures 1 to 4 the results of paper making properties on the pulps made using experiment 7.5 (Figures 1 and 2) and 7.6 (Comparative-Figures 3 and 4).

### Conclusions

The optimum pH of bleaching with TAED is around 8, but bleaching also succeeds at pH 6 to 6.5 (Table 6). Carrying out the process at temperature of around 80°C seems to give a slightly better result than at 60°C, except that the peroxide consumption tends to be higher (Table 1). Brightness gain is achieved with a 30 minute reaction time. Kappa reduction is further improved if the reaction time is extended to 120 minutes (Table 3). Kappa reduction is also improved by increasing dosages of TAED and peroxide, though the effect on brightness is minimal (Table 2). Surprisingly pulp brightness is improved where the incoming initial brightness is lower (i.e. pulp 1 compared to pulp 3). Pulp brightness reversion is improved by TAED under humid and dry conditions (PC,a and PC,b) (Table 6). The benefits of TAED remain even when the pulp is further bleached in a conventional alkaline peroxide stage (tests 7.5 and 7.6 and Table 5). TAED has no adverse effect on the physical properties of paper made from the pulp (Figures 1 to 4). Thus the improved colour reversion is obtained without trading-off against strength.

Trial	Peroxide Stage				
	Temp. °C	Initial/ Final pH	Reaction Time min	TAED Dose %	H2O2 dose/cons* %
1.1	60	6,3/6,4	120	-	2,0/0,08
1.2	60	6,4/4,5	120	0,67	2,0/0,10
1.3	80	6,3/6,6	120	-	2,0/0,02
1.4	80	6,2/4,4	120	0,67	2,0/0,35

Trial	Pulp Properties							
	Kappa Number	Absorption coeff. m <sup>2</sup> /kg	Light scatt. coeff. m <sup>2</sup> /kg	Brightness 457 nm %	PCa 457 nm	Brightness decrease, a %	PC, b 457 nm	Brightness decrease, b %
1.1	4,9	0,17	31,1	82,6	1,51	4,9	1,11	3,7
1.2	3,7	0,11	32,3	83,4	1,32	4,6	0,90	3,3
1.3	4,9	0,15	32,8	83,2	1,19	4,1	1,21	4,1
1.4	3,6	0,15	33,4	83,7	0,81	3,0	0,79	2,9

**TABLE 2 - The effect of peroxide and TAED doses on the bleaching result on Pulp No. 1**

Trial	Peroxide Stage					Pulp Properties					
	Temp. °C	Initial/ Final pH	Reaction Time min	TAED Dose %	H2O2 dose/cons* %	Kappa Number	Absorption coeff. m2/kg	Light seatt. coeff. m2/kg	Brightness 457 nm %	PCa 457 nm	Brightness decrease, a %
2.1	60	6,1/4,4	120	1,0	3,0/0,54	3,8	0,16	32,8	83,3	1,22	4,2
2.2	60	6,3/4,7	120	0,67	2,0/0,31	4,0	0,15	32,9	83,7	1,29	4,6
2.3	60	6,3/5,2	120	0,33	1,0/0,15	4,4	0,15	33,0	83,3	1,29	4,5

\* - consumption

**TABLE 3 - The effect of the reaction time on the bleaching result on Pulp No. 1**

Trial	Peroxide Stage					Pulp Properties		
	Temp. °C	Initial/ Final pH	Reaction Time min	TAED Dose %	H <sub>2</sub> O <sub>2</sub> dose/cons* %	Kappa Number	Absorption coeff. m <sup>2</sup> /kg	Brightness 457 nm %
3.1	60	6,2/4,7	120	0,67	2,0/0,22	4,1	0,15	83,6
3.2	60	6,2/4,8	60	0,67	2,0/0,22	4,3	0,14	83,5
3.3	60	6,2/5,4	30	0,67	2,0/0,14	4,7	0,14	83,5

\* - consumed

**TABLE 4 - The effect of pH in the acidic peroxide stage on Pulp No. 2**

Trial	Peroxide Stage			Pulp Properties				
	Temperature °C	Initial/final pH	TAED dose %	H2O2 cons* %	Kappa number	Absorption coeff. m2/kg	Light scatt coeff. m2/kg	Brightness 457 nm %
4.1	60	6,1/6,2	-	-	5,7			84,5
4.2	60	6,1/4,7	0,67	-	4,3			85,1
4.3	60	5,1/5,3	-	0,08	5,9			84,2
4.4	60	5,0/4,6	0,67	0,22	5,1			84,6
4.5	60	4,0/4,0	-	-	5,8			83,8
4.6	60	4,2/4,1	0,67	-	5,4			84,4
4.7	60	2,9/3,0	-	-	5,7			84,0
4.8	60	3,0/3,0	0,67	-	5,5			84,2
4.9	60	2,1/2,1	-	-	5,6	0,15	30,4	84,2
4.10	60	2,2/2,2	0,67	-	5,4	0,16	30,9	84,5

\* - consumed



**Table 5 - Use of TAED in the acidic and alkaline  
peroxide stages on Pulp No. 2**

Trial	Peroxide Stage					
	Temp °C	Initial/ final pH	0,1% DTPMP 0,24% MgSO <sub>4</sub>	Reaction Time min	TAED dose %	H <sub>2</sub> O <sub>2</sub> dose/cons* %
5.1	60	6,1/5,1	-	120	0,67	2,0/0,23
	20	10,1/10,1	-	120	0,67	2,0/0,25
5.2	60	6,1/5,1	-	120	0,67	2,0/0,23
	80	10,6/10,4	x	180	-	2,0/0,32
5.3	80	10,6/10,3	x	180	-	2,0/0,21

\* - consumed

TABLE 5 Cont'd

Trial	Pulp Properties									
	Kappa Number	Absorption coeff. m2/kg	Light scatt. coeff. m2/kg	B'ness 457 nm %	PC,a 457 nm	B'ness decrease a %	PC,b 457 nm	B'ness decrease a %	PC,c 457 nm	B'ness decrease, c %
5.1										
	4,7	0,11	30,4	85,9	0,94	4,1	1,31	5,4	0,83	3,7
5.2										
	4,5	0,10	31,3	87,5	0,68	3,5	1,13	5,4	0,63	3,3
5.3										
	5,6	0,12	31,1	86,1	1,00	4,4	1,46	6,1	0,67	3,1

**Table 6 - The effect of pH in the acidic and slightly alkaline peroxide stage on Pulp No. 3**

Trial	Peroxide Stage			
	Temperature °C	Initial/ Final pH	TAED Dose %	H <sub>2</sub> O <sub>2</sub> cons* %
6.1	60	2,1/2,1	-	-
6.2	60	2,1/2,1	0,67	0,30
6.3	60	4,0/4,1	-	-
6.4	60	3,9/3,8	0,67	0,21
6.5	60	6,5/6,5	-	-
6.6	60	6,3/4,8	0,67	0,24
6.7	60	8,1/7,7	-	-
6.8	60	8,1/5,8	0,67	0,41

\* - consumed

TABLE 6 Cont'd

Trial	Pulp Properties									
	Kappa Number	Absorption coeff. m <sup>2</sup> /kg	Light Scatt. coeff. m <sup>2</sup> /kg	Brightness 457nm %	PC,a 457 nm	Brightness decrease,a	PC,b 457 nm	Brightness decrease,b	PC,c 457 nm	Brightness decrease,c
6.1	2,1	0,17	32,3	84,5	0,21	0,9	0,48	2,0	0,66	2,7
6.2	2,1	0,19	32,6	84,1	0,28	1,2	0,51	2,1	0,73	2,9
6.3	2,2	0,15	31,3	84,6	0,25	1,1	0,55	2,3	0,72	3,0
6.4	2,0	0,16	32,1	84,9	0,26	1,2	0,57	2,5	0,63	2,7
6.5	2,1	0,21	31,1	85,0	0,27	1,2	0,53	2,3	0,64	2,7
6.6	1,7	0,15	30,4	85,7	0,27	1,3	0,48	2,2	0,65	2,9
6.7	2,1	0,15	31,4	85,4	0,24	1,1	0,65	2,8	0,75	3,3
6.8	1,9	0,13	30,8	86,4	0,23	1,2	0,50	2,4	0,68	3,2

**Table 7 - The effect of TAED and peroxide doses  
on Pulp No. 3.**

Trial	Peroxide Stage					
	Temp °C	Initial/ final pH	0,1% DTPMP 0,24% MgSO <sub>4</sub>	TAED Dose	H <sub>2</sub> O <sub>2</sub> dose/cons* %	Reaction Time min
7.1	60	6,3/5,5	-	0,1	0,3/0,04	360
7.2	60	6,3/4,8	-	0,67	2,0/0,24	120
7.3	60	6,3/4,3	-	1,3	4,0/0,47	120
7.4	60	6,1/4,3		2,0	6,0/0,68	120
7.5	60	6,5/4,9	-	0,67	2,0/0,25	120
7.6	80	10,4/10,2	x	-	2,0/-	180
	80	10,2/10,2	x	-	2,0/0,10	180

\* - consumed

TABLE 7 Cont'd

Trial	Kappa Number	Absorption coeff. m <sup>2</sup> /kg	Light scatt. coeff. m <sup>2</sup> /kg	Brightness 457 nm %	PC,a 457 nm	B'ness decrease,a %	PC,b 457 nm	B'ness decrease,a %	PC,c 457 nm	B'ness decrease, c
7.1	1,9	0,13	31,0	85,4						
7.2	1,7	0,15	30,4	85,7	0,27	1,3	0,48	2,2	0,65	2,9
7.3	1,6	0,15	32,5	86,0	0,25	1,3	0,39	2,0	0,60	2,9
7.4	1,5	0,15	32,8	86,4	0,28	1,5	0,44	2,3	0,58	2,9
7.5	1,9	0,14	28,6	85,8						
	1,5	0,11	30,2	88,5	0,17	1,2	0,34	2,3	0,59	3,6
7.6	1,9	0,13	30,8	87,2	0,23	1,4	0,45	2,6	0,57	3,1

CLAIMS

1. A process for bleaching cellulosic pulp comprising the steps:

(a) forming an aqueous solution containing hydrogen peroxide or an inorganic persalt or a bleach activator compound which is an acyl donor to form an oxidising compound which is a stronger oxidising agent than hydrogen peroxide, the steps being carried out at a pH in the range 1 to  $pK_a'$ ;

(b) contacting the pulp with the stronger oxidising agent at a starting pH in the range 1 to  $pK_a'$  where  $pK_a'$  is the  $pK_a$  of the percarboxylic acid corresponding to the acyl group of the activator,

in which the bleach activator compound is selected from N-acyl and O-acyl derivative and wherein when the activator compound is an anhydride it is a solid material.

2. A process for delignifying and/or bleaching cellulosic pulps comprising the steps:

(a) forming an aqueous solution containing hydrogen peroxide or an inorganic persalt and a bleach activator compound which is an acyl donor to form an oxidising compound which is a stronger oxidising agent than hydrogen peroxide, the step being carried out at a pH in the range 1 to  $pK_a'$ ;

(b) contacting the pulp with a stronger oxidising agent at a starting pH in the range 1 to  $pK_a'$  where  $pK_a'$  is the  $pK_a$  of the percarboxylic acid corresponding to the acyl group of the activator, in which the bleach activator compound is selected from N-acyl and O-acyl derivatives, and the hydrogen peroxide or inorganic persalt and the bleach activator compound are added directly to the pulp, either simultaneously or one after the other, the oxidising compound forming in the presence of the pulp.

3. A process according to claim 1 or claim 2 in which the pH in the step (b) is in the range  $(pK_a' - 5)$  to  $(pK_a' - 0.1)$ .

4. A process according to any preceding claim in which following step (b), the pulp is contacted with hydrogen

peroxide or other oxygen bleach at a pH in the range 9 to 12, optionally in the presence of an activator and/or sequestrant.

5     5. A process according to any preceding claim in which the pulp is recycled pulp.

6. A process according to any preceding claim in which the pulp, prior to step (b) has a brightness of less than 85% ISO.

10     7. A process according to any preceding claim in which the pulp is a paper-making pulp.

8. A process according to any preceding claim in which the concentration of hydrogen peroxide in step (a) is from 0.5% to 10% w/v.

15     9. A cellulosic product formed from pulp having a brightness of at least 85%, obtained by the process of any of claims 1 to 8.

10. Paper formed from a pulp bleached according to the process of any of claims 1 to 8.



# INTERNATIONAL SEARCH REPORT

Internat Application No  
PCT/G8 95/00246

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21C9/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 D21C C07C C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X, L	WO, A, 94 18297 (WARWICK INTERNATIONAL) 18 August 1994 see claims 1-19 ---	1-10
P, X	WO, A, 94 18298 (WARWICK INTERNATIONAL) 18 August 1994 see claims 1-18 ---	1-10
P, X	WO, A, 94 18299 (WARWICK INTERNATIONAL) 18 August 1994 see claims 1-24 ---	1-10
A	DE, A, 30 02 271 (VEB WASCHMITTELWERK GENTHIN) 30 July 1981 see claims 1-9 --- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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# INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/GB 95/00246

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 534 772 (WARWICK INTERNATIONAL) 31 March 1993 see claims 1-20 ---	1-10
A	EP,A,0 456 032 (HOECHST JAPAN LTD) 13 November 1991 cited in the application see claims 1-4 -----	1-10

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 95/00246

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		EP-A- 0605554	13-07-94
		WO-A- 9306203	01-04-93
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